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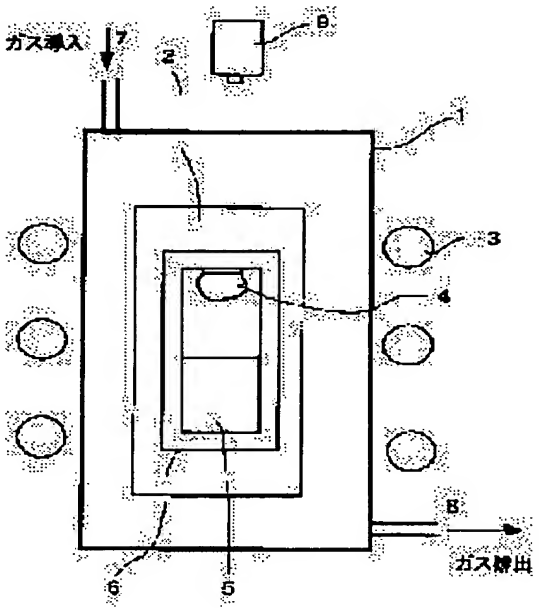
(54) METHOD FOR GROWING SILICON CARBIDE SINGLE CRYSTAL

(57)Abstract:
PROBLEM TO BE SOLVED: To develop a method for growing a single crystal for which silicon carbide powder is used as a raw material, which is free from the occurrence of void defects called micropipes, and which is almost free of screw dislocation and is of high-quality.
SOLUTION: The crystal is grown by a growing method for a silicon carbide single crystal where, in an inert atmosphere and under the condition that pressure is in the range of 100-300 Torr, a raw material is heated to 2,200-2,300° C that is 30-100° C lower than the raw material, and the growing speed of the single crystal substrate is adjusted to ≤70 μm/h. The crystal is also grown by a growing method for a silicon carbide single crystal where, in an inert atmosphere, an initially grown layer is formed while the initial temperature of the crystal substrate is made 2,250-2,350° C and a growing pressure is made 100-300 Torr, and then the crystal is grown while the substrate temperature and the growing pressure are decreased gradually and finally to 2,200-2,250° C and 1-20 Torr respectively.



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* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] The growth approach of the silicon carbide monocrystal characterized by heating [a pressure] 2250-2400 degrees C and the seed crystal substrate of silicon carbide for a silicon carbide powder raw material under the certain condition within the limits of 13.3-40kPa at 2200-2300 degrees C lower 30-100 degrees C than the temperature of a silicon carbide powder raw material, and adjusting and growing up the growth rate of a brown coal-ized silicon single crystal into 70 or less micrometer/h in an inert atmosphere.
[Claim 2] The growth approach of the silicon carbide monocrystal characterized by growing up silicon carbide monocrystal, reducing substrate temperature and a growth pressure gradually finally to the growth pressure 0.13 - 2.7kPa, and the substrate temperature of 2200-2250 degrees C in an inert atmosphere after forming 2250-2350 degrees C for the seed crystal substrate temperature of early silicon carbide and forming an initial growth phase for a growth pressure as 13.3-40kPa.
[Claim 3] The growth approach of silicon carbide monocrystal according to claim 2 that initial growth layer thickness is 70-300 micrometers.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] In case this invention carries out crystal growth of the silicon carbide monocrystal used for high pressure-proofing, a large power semiconductor device, etc. by the sublimating method, it relates to the crystal growth approach for growing up especially a high quality single crystal.
[0002]
[Description of the Prior Art] Silicon carbide has a high heat transfer coefficient and a low dielectric constant, thermally and chemically, it is an ingredient with the description that an energy band gap is stably large, and is compared with other semiconductor materials and can use them also under an elevated temperature as an usable environmental-proof component ingredient, a radiation-proof component ingredient, the power component ingredient for power control, and a short wavelength light emitting device ingredient. Moreover, the device using this is expected to be what can operate under the environment of the radiation consistency higher than the device manufactured from semiconductor materials by which current use is carried out, such as silicon (Si), which is high temperature. As an approach of manufacturing this silicon carbide monocrystal, the method of sublimating under an elevated temperature is usually used by using silicon carbide powder as a raw material.
[0003] In manufacture by the method of sublimating silicon carbide monocrystal, the crucible which installed the seed crystal substrate filled up with silicon carbide raw material powder in the inert gas ambient atmosphere is decompressed, and the temperature up of the whole equipment is carried out to 1800-2400 degrees C. In connection with a temperature up, steams, such as Si which contributes to crystal growth, Si2C, and SiC2, SiC, will occur from coal-for-coke-making-ized silicon, and it will float in the end crater which piles the particle of the impurity contained in a raw material etc. at coincidence, a crystalline active jamming particle, etc. When these impurity particle etc. adheres to the single crystal front face on which the seed crystal substrate which was made to counter the coal-for-coke-making-ized silicon layer in a crucible, and was formed grows, the crystal which grows epitaxial as a single crystal is told that they are generating of a micro pipe and the cause of a crystal rearrangement.
[0004] On the other hand, although fabrication is performed by grinding, washing, the chemical treatment, etc. in order to produce a seed crystal substrate from silicon carbide monocrystal, in this seed crystal substrate front face, disturbance, such as a deterioration layer produced at the time of processing, remains. Since silicon carbide is chemically stable, this damaged layer is difficult for there to be no suitable etchant and to remove. For this reason, by the usual sublimating method, many crystal defects, such as a micro pipe and screw dislocation, occur from a seed crystal substrate front face. Moreover, by the conventional sublimating method, in order that a crystal might grow according to spontaneous nucleation, control of the form of a crystal and the crystal face became difficult.
[0005] After growing up the crystal of high quality under the growth pressure of dozens kPa(s) in early stages of growth, the pressure is dwindled to 0.13-1.3kPa, and it is made to grow up, in order to solve this (JP,59-35099,A). Moreover, the reduced pressure approach by two or more steps is proposed as an approach of dwindling a pressure in JP,11-60390,A as this improvement patent. The crystal defect which originates in seed crystal by the approach of stopping low these initial rates of crystal growth of growth was controlled, the initial growth phase was made into quality silicon carbide monocrystal, and the quality improvement of a crystal which grows after it is measured.
[0006] However, although the crystal with any approach quality in early stages of late growth of a growth rate is obtained, when a pressure is made low and a growth rate is gathered, crystal defects, such as screw dislocation, are occurring. Moreover, probably because crystal skin temperature changes with crystal growth, the degree of supersaturation on the front face of growth changes similarly, it does not become stable crystal growth but a crystal defect and a polymorphism are easy to be intermingled for this reason in connection with this

disturbance.
[0007]
[Problem(s) to be Solved by the Invention] This invention uses silicon carbide powder as a raw material, does not have generating of the defect of the shape of a cavity called a micro pipe, and aims at development of the growth approach of very few quality single crystals of screw dislocation.
[0008]
[Means for Solving the Problem] This invention [1] In an inert atmosphere, a pressure is set under the certain condition within the limits of 13.3-40kPa. A silicon carbide powder raw material 2250 degrees C - 2400 degrees C, The seed crystal substrate of silicon carbide is heated at 2200-2300 degrees C lower 30-100 degrees C than the temperature of a silicon carbide powder raw material. And the growth approach of the silicon carbide monocrystal characterized by adjusting and growing up the growth rate of silicon carbide monocrystal into 70 or less micrometer/h [2] In an inert atmosphere After forming 2250-2350 degrees C for the seed crystal substrate temperature of early silicon carbide and forming an initial growth phase for a growth pressure as 13.3-40kPa, Finally substrate temperature and a growth pressure Growth pressure 0.13-2.7kPa, The growth approach of the silicon carbide monocrystal characterized by growing up silicon carbide monocrystal, reducing gradually to the substrate temperature of 2200-2250 degrees C, And [3] The above-mentioned technical problem was solved by developing the growth approach of silicon carbide monocrystal according to claim 2 that initial growth layer thickness is 70-300 micrometers.
[0009]
[Embodiment of the Invention] As equipment used for growth of the silicon carbide monocrystal of this invention, it is kept warm with a heat insulator, for example in a vacuum housing, and the crucible made from a graphite whose heating was enabled by the RF etc. from the exterior is used. Heating apparatus mainly heats the crucible base filled up with silicon carbide raw material powder, and it is formed so that the seed crystal substrate and heat gradient of silicon carbide which were prepared in the top surface lower part which countered it can be adjusted.
[0010] In order to prevent the pyrolysis of silicon carbide on the occasion of crystal growth, the ambient atmosphere in a crucible needs to carry out under inert gas ambient atmospheres, such as an argon and helium. It is gas by which it saw from the point of cost and effectiveness, and the argon balanced most. After setting a raw material and seed crystal, the ambient atmosphere in a crucible is made into a vacuum once nearly completely, it is re-filled up with a high grade argon up to dozens kPa(s) next, if still more nearly required, will repeat this and will make it an inert atmosphere by adjusting to the pressure of the ambient atmosphere which needs by performing inert gas replacement enough.
[0011] A silicon carbide powder raw material has the desirable thing of a high grade with a natural thing, in order to create the silicon carbide monocrystal of high quality. Since impurities contained in coal-for-coke-making-ized silicon with the sublimation gas of a silicon carbide raw material in a raw material when there are many impurities, such as Fe and Ti, and the active jamming minute particle which, in addition to this, bars the crystal growth of high quality will carry out abundant suspension into a crucible, although crystal form is not asked, it is desirable that it is the silicon carbide of a high grade.
[0012] As indicated previously, the silicon carbide substrate used as a seed crystal substrate needs to produce from silicon carbide monocrystal. The silicon carbide monocrystal of the high quality of the crystal form to need is cut and ground, and it considers as a configuration required as seed crystal. Subsequently, by washing by the hydrofluoric acid, in order to remove the deterioration layer in which crystal form including the disturbance by cutting and polish in a front face was confused as much as possible (for example, after heat concentrated sulfuric acid's washing, and the mixture of aqueous ammonia and a hydrogen peroxide washing subsequently, washing by deionized water and annealing at an about 1200-degree C elevated temperature under an oxygen ambient atmosphere in order to remove an oxide film), disturbance is removed and it considers as seed crystal. Since disturbance is not completely removed yet even if such, it is necessary to consider as the conditions [like] which erase such disturbance in initial growth (it is made small).
[0013] While a growth rate becomes large so that the seed crystal substrate heating unit of silicon carbide generally makes growth temperature high in 2200 degrees C or more, the inclination of an increment also has generating of the cavity-like defect of a crystal, and generation of screw dislocation, but even if it becomes 2200 degrees C or less, the phenomenon of control of generating of a cavity-like defect or generation of screw dislocation does not appear so clearly so much. Therefore, when taking productivity into consideration, it is desirable to make seed crystal substrate heating unit temperature of silicon carbide into 2200 degrees C or more.
[0014] As for the growth rate of a single crystal, a growth rate becomes large, so that growth temperature is high. Moreover, a growth rate becomes large, so that the pressure of an ambient atmosphere is low. The grace of

a crystal falls, so that a growth rate is large still more generally.

[0015] In invention of the above [1], it is the approach of adjusting a growth rate to 70 or less micrometer/hr, and growing up silicon carbide monocrystal, under a pressure 13.3 - 40kPa, the silicon carbide powder raw material temperature of 2250-2400 degrees C, and the fixed condition that held the seed crystal substrate of silicon carbide to temperature lower 30-100 degrees C than this. Even when growing up this single crystal and the disturbance of the some of seed crystal remains, the silicon carbide monocrystal of high quality can be manufactured. In addition, since the growth rate of a single crystal cannot be measured directly, it needs to carry out measuring of the relation of a pressure and temperature beforehand, and to adjust to a predetermined growth rate.

[0016] In the growth approach of the silicon carbide monocrystal invention the above [2] the seed crystal substrate temperature of early silicon carbide 2250-2350 degrees C, It is an initial growth phase (about 70-300 micrometers as thickness) considering a pressure as 13.3-40kPa. After forming 100-200 micrometers preferably, finally temperature and a pressure Pressure 0.13-2.7kPa, When growing up a crystal, reducing gradually to the substrate temperature of 2200-2250 degrees C, control of generating of a cavity-like defect and generation of screw dislocation can be pressed down greatly, and can manufacture the single crystal of high quality.

[0017] Especially in invention of the above [2] of this invention, when carrying out [cm] the temperature gradient between the silicon carbide raw material heating unit in a growth process, and the seed crystal heating unit of silicon carbide in about 20-60 degrees C /, since there is no generating of a micro pipe that a growth rate is large in a surprising thing and generating of a crystal rearrangement can be decreased greatly, it is a desirable temperature gradient. Consequently, it became possible to manufacture the silicon carbide monocrystal of high quality as it is also at a comparatively large growth rate.

[0018] In growth of silicon carbide monocrystal, when maintaining an elevated temperature 2200 degrees C or more lower [temperature / of silicon carbide / seed crystal substrate] 30-100 degrees C than silicon carbide raw material temperature, the surface migration of the raw material molecule adhering to a substrate front face becomes active, and the part into which it not only controls unnecessary secondary karyogenesis, but sublimation recrystallization of a single crystal substrate front face also became active, and the front face was in disorder is reconfigurated. The crystal defect represented by the screw dislocation conventionally generated from the single crystal substrate front face according to these operations is controlled. It is necessary to set a surrounding pressure to 13.3 or more kPas so that a degree of supersaturation may not become excessive, and it is necessary to make it 70 or less micrometer/h as a growth rate at this time. Moreover, after forming an initial growth phase, in making a growth rate into hundreds micrometer/h, it lowers a surrounding pressure gradually. At this time, the temperature on the front face of a crystal becomes high in connection with crystal growth. When temperature becomes high too much, a sublimation operation of a crystal front face becomes strong, and a crystal receives a damage. The defect generated during a crystal can be controlled by decompressing to coincidence, adjusting seed single crystal substrate temperature, in order to ease this. There is no generating of the defect of the shape of a cavity called the micro pipe which had hundreds of number 10-piece [/cm] 2 by this, and screw dislocation is also reduced from 2 sharply [cm] 103-104 pieces /to 2 cm by 105-106 pieces /.

[0019]

[Example] (Example 1) An example of the crystal growth equipment by this invention is shown in drawing 1 . The end crater which gets bore a depth of 95mm of 50mm which consists of a graphite was filled up with silicon carbide raw material powder (Showa Denko # 240) so that it might become in height of 60mm. the crucible lid inferior surface of tongue made from a graphite — Rayleigh — it was created by law — about 1cm, the 6H-silicon carbide monocrystal of 2 was stuck as a seed crystal substrate (0.5mm in a 6H-silicon-carbide-monocrystal (Si) side, the diameter of 10mm, thickness), and was held. This lid has been arranged to crucible opening and this graphite crucible was set to the coil in a package high-frequency-heating furnace with the heat insulator. After being filled up with the reaction within the pipe one reduced pressure-back to 6.7x10-7kPa from gas exhaust 8 and being filled up with argon gas from the inert gas inlet 7 to ordinary pressure, again, from gas exhaust, it decompressed to 6.7x10-7kPa, and the air within between reactions was driven out. And a temperature up is carried out until it is again filled up with argon gas from an inert gas inlet to 93kPa(s) and becomes 2200 degrees C about 2250 degrees C and seed crystal substrate temperature in silicon carbide powder raw material temperature.

[0020] From the blasting-fumes exhaust port, gas was discharged, where the argon ambient pressure force is decompressed to 13.3kPa(s), silicon carbide monocrystal was grown up for 72 hours, and silicon carbide monocrystal with a die length of 3mm was obtained as a growth phase. Growth rates were 3mm / 72h**40 micrometer/h. In this case, that difference was 50 degrees C at the substrate temperature of 2200 degrees C, and the raw material temperature of 2250 degrees C, and since spacing of a raw material powder side and a seed

crystal substrate was set to 2.5cm, the temperature gradient was 20 degrees C/cm. To the growth direction, perpendicularly, mirror polishing was carried out, and cutting and when it observed with the transparency polarization microscope, the micro pipe had not generated this crystal. Moreover, when it dipped in the 500-degree C melting KOH for 10 minutes and etch pit observation was carried out, the quality crystal [consistency / etch pit] 4x103 pieces /2 was obtained cm. Moreover, it checked that the polymorphism crystal was not intermingled according to an X diffraction.

[0021] (Example 2) In the example 1, after being again filled up with argon gas from the inert gas inlet to 93kPa (s), condition adjustment was performed to the silicon carbide powder raw material temperature of 2400 degrees C, the seed crystal substrate temperature of 2300 degrees C, and growth pressure 13.3kPa as growth conditions for an initial growth phase, and crystal growth was performed on the condition for 3 hours. Growth was performed for 20 hours, reducing substrate temperature and a pressure gradually, discharging gas from the blasting-fumes exhaust port. Final substrate temperature was 2200 degrees C (silicon carbide powder raw material temperature of 2300 degrees C), and growth pressures were 0.13kPa(s). Nitrogen gas is mixed in a growth controlled atmosphere in the place to which it began to change substrate temperature and a pressure, a silicon carbide crystal is colored, and the location which changed understood growth conditions.

[0022] Consequently, in initial growth, silicon carbide monocrystal with a die length of about 200 micrometers was obtained. Growth rates are 200 micrometers / 3h= about 67 micrometer/h. Moreover, since it begins to have reduced substrate temperature and a growth pressure, the 2.8mm single crystal was grown up in 20 hours. Average growth rates were 2.8mm / 20h=140 micrometer/h. Moreover, the difference of the substrate temperature in this case and raw material temperature was 100 degrees C, and since spacing between a raw material and seed crystal was set to 2.5cm, the temperature gradient was 40 degrees C/cm. To the growth direction, perpendicularly, mirror polishing was carried out, and cutting and when it observed with the transparency polarization microscope, the micro pipe had not generated this crystal. Moreover, when it dipped in the 500-degree C melting KOH for 10 minutes and etch pit observation was carried out, the quality crystal [consistency / etch pit] 6x103 pieces /2 was obtained cm. Moreover, it checked that dislocation density was small also in an X-ray topogrph.

[0023]

[Effect of the Invention] Also in the inside of crystal growth, without being influenced by this invention by the turbulence and dirt of a crystal which exist in a seed crystal substrate front face, it becomes possible to continue stable growth and crystal defects, such as a rearrangement in a growth process, become is hard to be introduced into silicon carbide monocrystal. Thereby by the former, the cavity-like defect of generating of a micro pipe called a micro pipe is lost from dozens in this invention to hundreds of pieces /having occurred two times cm. Moreover, 105-106 defects [103-104 / /] /which influence the semiconductor device property called screw dislocation are also improvable [to 2] from 2 cm cm by defect density.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The sectional view of the equipment used for the example.
[Drawing 2] TOPOGURAFU of the growth crystal by this invention.
[Drawing 3] TOPOGURAFU of the growth crystal by the conventional method.
[Description of Notations]
1 Vacuum Housing
2 Heat Insulator
3 High Frequency Coil
4 Growth Crystal
5 Silicon Carbide Raw Material Powder
6 Graphite Crucible
7 Gas Inlet
8 Gas Exhaust
9 Radiation Thermometer

[Translation done.]

#7195

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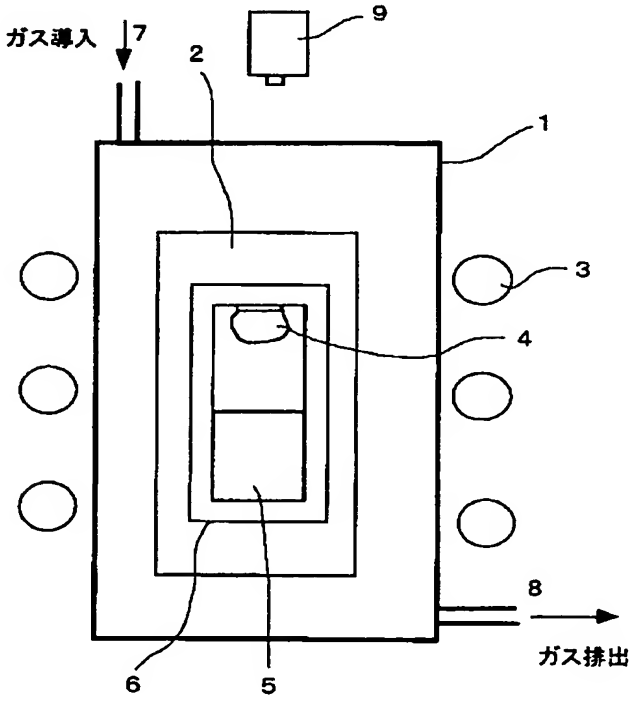
最終頁に続く

(54)【発明の名称】　炭化珪素単結晶の成長方法

(57)【要約】
【課題】　炭化珪素粉末を原料とし、マイクロパイプと呼ばれる空洞状の欠陥の発生がなく、螺旋転位の極めて少ない高品質な単結晶の成長方法の開発の提供。
【解決手段】　不活性雰囲気において、圧力を１００～３００Ｔｏｒｒの範囲内の条件下において原料を２２５０℃から２４００℃、種単結晶基板を原料の温度より３０～１００℃低い２２００～２３００℃に加熱し、かつ単結晶基板の成長速度を７０μｍ／ｈ以下に調整して成長させる炭化珪素単結晶の成長方法および不活性雰囲気において、初期の結晶基板温度を２２５０から２３５０℃、成長圧力を１００～３００Ｔｏｒｒとして初期成長層を形成した後、基板温度および成長圧力を減じながら最終的に成長圧力１～２０Ｔｏｒｒ、温度２２００～２２５０℃まで徐々に減じながら結晶を成長させる炭化珪素単結晶の成長方法。



【特許請求の範囲】
【請求項１】　不活性雰囲気において、圧力を１３．３～４０ｋＰａの範囲内の一定の条件下において炭化珪素粉末原料を２２５０～２４００℃、炭化珪素の種結晶基板を炭化珪素粉末原料の温度より３０～１００℃低い２２００～２３００℃に加熱し、かつ炭化珪素単結晶の成長速度を７０μｍ／ｈ以下に調整して成長させることを特徴とする炭化珪素単結晶の成長方法。
【請求項２】　不活性雰囲気において、初期の炭化珪素の種結晶基板温度を２２５０～２３５０℃、成長圧力を１３．３～４０ｋＰａとして初期成長層を形成した後、基板温度および成長圧力を最終的に成長圧力０．１３～２．７ｋＰａ、基板温度２２００～２２５０℃まで徐々に減じながら炭化珪素単結晶を成長させることを特徴とする炭化珪素単結晶の成長方法。
【請求項３】　初期成長層の厚さが７０～３００μｍである請求項２に記載の炭化珪素単結晶の成長方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は高耐圧、大電力用半導体素子等に使用される炭化珪素単結晶を昇華法により結晶成長させる際に，特に高品質単結晶を成長させるための結晶成長方法に関する。
【０００２】
【従来の技術】炭化珪素は、高い伝熱係数、低い誘電率を有し、熱的、化学的に安定でかつエネルギーバンドギャップが広い特徴を持つ材料であり、他の半導体材料に比し高温下でも使用可能な耐環境素子材料、耐放射線素子材料、電力制御用パワー素子材料、短波長発光素子材料として利用できる。またこれを用いたデバイスはシリコン（Ｓｉ）など現在使用されている半導体材料から製造したデバイスよりも高温度でかつ高い放射線密度の環境下で作動できるものと予期される。この炭化珪素単結晶を製造する方法としては、通常炭化珪素粉末を原料として高温下での昇華法が用いられている。
【０００３】炭化珪素単結晶の昇華法による製造においては、不活性ガス雰囲気中で炭化珪素原料粉末を充填した種結晶基板を設置したるつぼを減圧し、装置全体を１８００～２４００℃に昇温する。昇温に伴い原料炭化珪素からは結晶成長に寄与するＳｉ、Si_2C、SiC_2、ＳｉＣなどの蒸気が発生し、同時に原料などに含まれる不純物の微粒子、結晶性の妨害微粒子等もるつぼ内に浮遊することになる。るつぼ内の原料炭化珪素層に対向させて設けた種結晶基板の成長する単結晶表面に、これら不純物微粒子などが付着することにより単結晶としてエピタキシャルに成長する結晶にマイクロパイプの発生、結晶転位の原因となっているといわれている。
【０００４】一方、炭化珪素単結晶から種結晶基板を作製するため、研削、洗浄、薬品処理などにより成形加工が行われるが、この種結晶基板表面には加工時に生じた変質層等の外乱が残存している。この加工変質層は炭化珪素が化学的に安定であるため適切なエッチャントが無く除去することが困難となっている。このため通常の昇華法では、マイクロパイプや螺旋転位等といった結晶欠陥が種結晶基板表面から数多く発生してくる。また、従来の昇華法では自然発生的な核形成により結晶が成長するため結晶の形および結晶面の制御が困難なものとなっていた。
【０００５】これを解決するために、成長初期に数十ｋＰａの成長圧力下で高品質の結晶を成長させた後、その圧力を０．１３～１．３ｋＰａまで漸減させ成長させている（特開昭５９－３５０９９号公報）。またこの改良特許として特開平１１－６０３９０号公報においては圧力を漸減させる方法として複数段階による減圧方法が提案されている。これらの成長初期結晶成長速度を低く抑える方法によって種結晶に由来する結晶欠陥を抑制し、初期成長層を高品質な炭化珪素単結晶とし、それ以後成長する結晶の高品質化を計っている。
【０００６】しかしながら、いずれの方法も成長速度の遅い成長初期には高品質な結晶が得られているものの、圧力を低くし成長速度を増した時点で螺旋転位等の結晶欠陥が発生してきている。また、結晶の成長とともに結晶表面温度が変化するためか成長表面の過飽和度も同様に変化し、このため、安定な結晶成長にならずこの外乱に伴って結晶欠陥や多形が混在しやすくなっている。
【０００７】
【発明が解決しようとする課題】本発明は、炭化珪素粉末を原料とし、マイクロパイプと呼ばれる空洞状の欠陥の発生がなく、螺旋転位の極めて少ない高品質な単結晶の成長方法の開発を目的とするものである。
【０００８】
【課題を解決するための手段】本発明は、［１］　不活性雰囲気において、圧力を１３．３～４０ｋＰａの範囲内の一定の条件下において炭化珪素粉末原料を２２５０℃～２４００℃、炭化珪素の種結晶基板を炭化珪素粉末原料の温度より３０～１００℃低い２２００～２３００℃に加熱し、かつ炭化珪素単結晶の成長速度を７０μｍ／ｈ以下に調整して成長させることを特徴とする炭化珪素単結晶の成長方法、［２］　不活性雰囲気において、初期の炭化珪素の種結晶基板温度を２２５０～２３５０℃、成長圧力を１３．３～４０ｋＰａとして初期成長層を形成した後、基板温度および成長圧力を最終的に成長圧力０．１３～２．７ｋＰａ、基板温度２２００～２２５０℃まで徐々に減じながら炭化珪素単結晶を成長させることを特徴とする炭化珪素単結晶の成長方法、および［３］　初期成長層の厚さが７０～３００μｍである請求項２に記載の炭化珪素単結晶の成長方法、を開発することにより上記の課題を解決した。
【０００９】
【発明の実施の形態】本発明の炭化珪素単結晶の成長に

使用する装置としては、例えば真空容器内に断熱材で保温され、外部より高周波などにより加熱可能とした黒鉛製のるつぼを使用する。加熱装置は炭化珪素原料粉末を充填したるつぼ底面を主として加熱し、それに対向した蓋面下部に設けられた炭化珪素の種結晶基板と熱勾配を調整できるように設けられている。

【００１０】結晶の成長に際し、炭化珪素の熱分解を防ぐためるつぼ内の雰囲気はアルゴン、ヘリウムなどの不活性ガス雰囲気下で行うことが必要である。コストおよび効果の点から見てアルゴンが最もバランスしたガスである。るつぼ内の雰囲気は、原料、、種結晶をセットした後、一旦ほぼ完全に真空にし、次に高純度アルゴンを数十ｋＰａまで再充填し、さらに必要ならばこれを繰り返して十分ガス置換を行い、必要とする雰囲気の圧力に調整することにより不活性雰囲気とする。

【００１１】炭化珪素粉末原料は、高品質の炭化珪素単結晶を作成するためには当然のことながら高純度のものが好ましい。原料中に不純物が多いときは炭化珪素原料の昇華ガスとともに原料炭化珪素に含まれるＦｅ、Ｔｉ等の不純物や、その他高品質の結晶の成長を妨げる妨害微小粒子がるつぼ内に多量浮遊することになるので、結晶形は問わないが高純度の炭化珪素であることが好ましい。

【００１２】先に記載したように、種結晶基板とする炭化珪素基板は、炭化珪素単結晶から作製することが必要である。必要とする結晶形の高品質の炭化珪素単結晶を切削、研磨して種結晶として必要な形状とする。ついで表面にある切削、研磨による外乱を含む結晶形の乱れた変質層をできるだけ除くため、例えば熱濃硫酸で洗浄し、ついでアンモニア水と過酸化水素の混合物で洗浄し、脱イオン水で洗浄し、酸素雰囲気下で１２００℃程度の高温で焼鈍した後、酸化膜を除去するためフッ化水素酸で洗浄することにより外乱を除去して種結晶とする。このようにしてもまだ完全に外乱は除去されていないので、初期成長においてこれらの外乱を消す（小さくする）様な条件とすることが必要となる。

【００１３】一般に炭化珪素の種結晶基板加熱部が２２００℃以上においては、成長温度を高くするほど成長速度が大きくなる反面、結晶の空洞状欠陥の発生や螺旋転位の生成も増加の傾向にあるが、２２００℃以下になってもさほど空洞状欠陥の発生の抑制や螺旋転位の生成の現象はさほど明確には表れない。従って生産性を考慮するときは炭化珪素の種結晶基板加熱部温度を２２００℃以上とすることが好ましい。

【００１４】単結晶の成長速度は、成長温度が高いほど成長速度が大きくなる。また雰囲気の圧力が低いほど成長速度は大きくなる。さらに一般的には成長速度が大きいほど結晶の品位は低下する。

【００１５】前記［１］の発明においては、圧力１３．３～４０ｋＰａ、炭化珪素粉末原料温度２２５０～２４００℃、炭化珪素の種結晶基板をこれより３０～１００℃低い温度に保持した一定条件下、成長速度を７０μｍ／ｈｒ以下に調整して炭化珪素単結晶を成長させる方法である。かかる単結晶の成長を行うときは、種結晶の若干の外乱が残っていたときでも、高品質の炭化珪素単結晶を製造できる。なお単結晶の成長速度は直接測定不可能であるので、あらかじめ圧力、温度の関係を検量しておき所定の成長速度に調整することが必要である。

【００１６】前記［２］の発明の炭化珪素単結晶の成長方法において、初期の炭化珪素の種結晶基板温度が２２５０～２３５０℃、圧力を１３．３～４０ｋＰａとして初期成長層（厚さとして約７０～３００μｍ、好ましくは１００～２００μｍ）を形成した後、温度および圧力を最終的に圧力０．１３～２．７ｋＰａ、基板温度２２００～２２５０℃まで徐々に減じながら結晶を成長させる時は、空洞状欠陥の発生の抑制や螺旋転位の生成は大きく押さえることができ、高品質の単結晶を製造できる。

【００１７】特に本発明の前記［２］の発明においては、成長工程における炭化珪素原料加熱部と炭化珪素の種結晶加熱部間の温度勾配を約２０～６０℃／ｃｍにするときは、驚くべきことには成長速度が大きくともマイクロパイプの発生がなく、また結晶転位の発生を大きく減少できるので好ましい温度勾配である。この結果、比較的大きい成長速度でもって高品質の炭化珪素単結晶を製造することが可能となった。

【００１８】炭化珪素単結晶の成長において、炭化珪素の種結晶基板温度を炭化珪素原料温度よりも３０～１００℃低くかつ２２００℃以上の高温を維持する時は、基板表面に付着した原料分子の表面マイグレーションが活発になり、不要な２次核発生を抑制するだけでなく、単結晶基板表面の昇華再結晶化も活発になり表面の乱れた部分が再構成される。これらの作用により従来単結晶基板表面から発生していた螺旋転位等に代表される結晶欠陥は抑制される。この時、過飽和度が過度にならないよう周囲の圧力を１３．３ｋＰａ以上にし、成長速度として７０μｍ／ｈ以下にする必要がある。　また初期成長層を形成した後、成長速度を数百μｍ／ｈにする場合には徐々に周囲の圧力を下げる。この時、結晶成長に伴い結晶表面の温度が高くなる。過度に温度が高くなる場合には、結晶表面の昇華作用が強くなり結晶がダメージを受ける。これを緩和するために種単結晶基板温度を調節しながら同時に減圧を行うことにより、結晶中に発生する欠陥を抑制することが出来る。これにより数十～数百個／ｃｍ^{2}あったマイクロパイプと呼ばれる空洞状の欠陥の発生はなく螺旋転位も10^5～10^6個／ｃｍ^{2}から10^3～10^4個／ｃｍ^{2}に大幅に低減されている。

【００１９】

【実施例】（実施例１）本発明による結晶成長装置の一例を図１に示す。黒鉛からなる内径５０ｍｍ深さ９５ｍ

mのるつぼに炭化珪素原料粉末（昭和電工製＃２４０）を高さ６０mmになるよう充填した。黒鉛製るつぼ蓋下面にはレーリー法で作成された約１ｃｍ２の６Ｈ－炭化珪素単結晶を種結晶基板（６Ｈ－炭化珪素単結晶（Ｓｉ）面、１０mm径、厚さ０．５mm）として貼り付け保持した。この蓋をるつぼ開口部に配置し、この黒鉛るつぼを断熱材で包み高周波加熱炉内の反応管にセットした。ガス排出口８より反応管内を６．７×10^{-7}ｋＰａに減圧後、不活性ガス導入口７よりアルゴンガスを常圧まで充填した後、再度ガス排出口より６．７×10^{-7}ｋＰａまで減圧し反応間内の空気を追い出した。そして不活性ガス導入口よりアルゴンガスを再度９３ｋＰａまで充填し、炭化珪素粉末原料温度を２２５０℃、種結晶基板温度を２２００℃になるまで昇温する。

【００２０】その後ガス排出口よりガスを排出し、アルゴン雰囲気圧力を１３．３ｋＰａに減圧した状態で炭化珪素単結晶の成長を７２時間行い、成長層として長さ３mmの炭化珪素単結晶を得た。成長速度は３mm／７２ｈ≒４０μｍ／ｈであった。この場合基板温度２２００℃、原料温度２２５０℃でその差は５０℃であり、原料粉末面と種結晶基板との間隔は２．５ｃｍとしたので温度勾配は２０℃／ｃｍであった。この結晶を成長方向に対して垂直に切断、鏡面研磨し、透過偏光顕微鏡で観察したところマイクロパイプは発生していなかった。また、５００℃の溶融ＫＯＨに１０分間浸し、エッチピット観察をしたところ、エッチピット密度が４×10^{3}個／ｃm^{2}という高品質な結晶が得られた。また、Ｘ線回折により多形結晶が混在していないことを確認した。

【００２１】（実施例２）実施例１において、不活性ガス導入口よりアルゴンガスを再度９３ｋＰａまで充填した後、初期成長層の成長条件として炭化珪素粉末原料温度２４００℃、種結晶基板温度２３００℃、成長圧力１３．３ｋＰａに条件調整を行い、その条件で３時間結晶成長を行った。その後ガス排出口よりガスを排出しながら、基板温度および圧力を徐々に減じながら２０時間成長を行った。最終的な基板温度は２２００℃（炭化珪素粉末原料温度２３００℃）、成長圧力は０．１３ｋＰａであった。基板温度および圧力を変化させ始めたところで成長雰囲気ガスに窒素ガスを混入して炭化珪素結晶を着色し、成長条件を変化した位置が分かるようにした。

【００２２】その結果、初期成長では約２００μmの長さの炭化珪素単結晶を得た。成長速度は２００μｍ／３ｈ＝約６７μｍ／ｈである。また基板温度および成長圧力を減じ始めてからは、２０時間で２．８mmの単結晶を成長させた。平均の成長速度は２．８mm／２０ｈ＝１４０μｍ／ｈであった。またこの際の基板温度と原料温度の差は１００℃であり、原料と種結晶との間の間隔は２．５ｃｍとしたので温度勾配は４０℃／ｃｍであった。この結晶を成長方向に対して垂直に切断、鏡面研磨し、透過偏光顕微鏡で観察したところマイクロパイプは発生していなかった。また、５００℃の溶融ＫＯＨに１０分間浸し、エッチピット観察をしたところ、エッチピット密度が６×10^{3}個／ｃm^{2}という高品質な結晶が得られた。また、Ｘ線トポグラフにおいても転位密度が小さくなっていることを確認した。

【００２３】

【発明の効果】本発明により，種結晶基板表面に存在する結晶の乱れや汚れに影響されること無く、また結晶成長中も安定な成長を続けることが可能となり成長過程における転位等の結晶欠陥が炭化珪素単結晶中に導入されにくくなる。これにより従来ではマイクロパイプと呼ばれる空洞状欠陥が数十から数百個／ｃm^{2}発生していたのに対し本発明においてはマイクロパイプの発生はなくなる。また、螺旋転位と呼ばれる半導体素子特性に影響する欠陥も欠陥密度で10^{5}～10^{6}個／ｃm^{2}から10^{3}～10^{4}個／ｃm^{2}に改善することができる。

【図面の簡単な説明】

【図１】実施例に使用した装置の断面図。

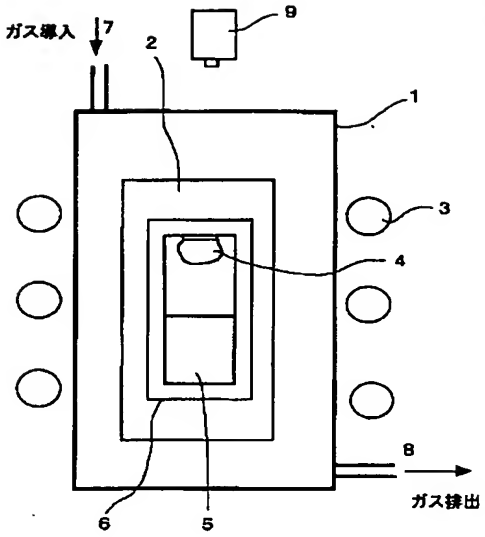
【図２】本発明による成長結晶のトポグラフ。

【図３】従来法による成長結晶のトポグラフ。

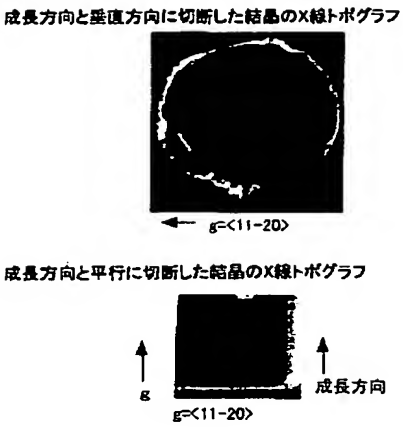
【符号の説明】

１　真空容器
２　断熱材
３　高周波コイル
４　成長結晶
５　炭化珪素原料粉
６　黒鉛るつぼ
７　ガス導入口
８　ガス排出口
９　放射温度計

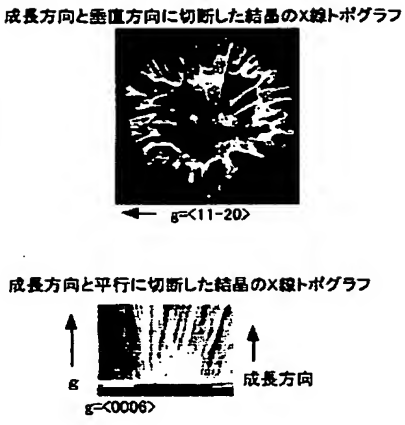
【図１】



【図２】



【図３】



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